

Catalytic Tri-reforming of Methane Using Flue Gas from Fossil Fuel-based Power Plants

Wei Pan, Jian Zheng, Chunshan Song*

Clean Fuels and Catalysis Program, Energy Institute and
Department of Energy & Geo-Environmental Engineering,
The Pennsylvania State University, University Park, PA 16802
*Email: csong@psu.edu; Tel: 814-863-4466; Fax: 814-865-3248

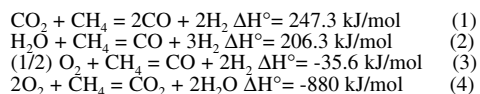
Introduction

The present work is an exploratory study on a new process for the production of synthesis gas ($\text{CO} + \text{H}_2$) using CO_2 in flue gas from fossil fuel-based electric power plants. The existing processes for synthesis gas production from methane or natural gas include steam reforming, CO_2 reforming, auto-thermal reforming, and partial oxidation, of methane or natural gas. The new process is called tri-reforming of methane, referring to simultaneous oxy- CO_2 -steam reforming.

Tri-reforming is a new process designed for the direct production of synthesis gas with desirable H_2/CO ratios by reforming methane or natural gas using flue gas from fossil fuel-based electric power plants without pre-separation of CO_2 . These flue gases are regarded as major source of CO_2 emission in the U.S. Generally the compositions of flue gases depend on the types of fossil fuels used in power plants. Flue gases from natural gas-fired power plants typically contain 8-10% CO_2 , 18-20% H_2O , 2-3% O_2 , and 67-72% N_2 ; flue gases from coal-fired boilers primarily contain 12-14% CO_2 , 8-10% H_2O , 3-5% O_2 , 72-77% N_2 , and trace amount of NO_x , SO_x , and particulates [1].

It is hypothesized that tri-reforming be a synergetic combination of CO_2 reforming (Eq.1), steam reforming (Eq. 2), and methane oxidation reactions (Eqs. 3 and 4). Therefore, tri-reforming is expected to encompass a number of unique features. One major feature is its ability to convert CO_2 in flue gas without CO_2 separation while avoiding the use of pure CO_2 and the severe problem of carbon deposition encountered in CO_2 reforming system [2-6]. Currently most of pure CO_2 is obtained from CO_2 separation processes (e.g. absorption, adsorption, and membrane separation) that are often energy-intensive and costly. Some separation processes could lower the power plant energy output as much as 20% [7].

Other features of tri-reforming include that there is no need to handle pure oxygen and it directly produces synthesis gas with a desirable H_2/CO ratio (e.g. $\text{H}_2/\text{CO} = 1.5 \sim 2$). Furthermore, oxygen in flue gas may help to ease the reaction energy requirement as encountered in CO_2 reforming alone or steam reforming alone. In general, the new tri-reforming process concept is consistent with the goals of DOE Vision 21 for power plants with respect to decreasing greenhouse gas emission, improving power generation efficiency and co-producing fuels and chemicals [8].



It should be pointed out that the H_2/CO ratio in synthesis gas is important since synthesis gas with different H_2/CO ratios has different applications in industry. The current major applications of synthesis gas (not hydrogen) include methanol synthesis and Fischer-Tropsch (F-T) synthesis that require synthesis gas with a H_2/CO ratio close to 2. However, synthesis gas directly produced from CO_2 reforming of methane has H_2/CO ratio close to 1. Hence this kind of synthesis gas (H_2/CO ratio ≤ 1) requires further treatment in order to be applied in methanol and F-T synthesis.

Similarly synthesis gas produced from steam reforming can not be directly applied in methanol or F-T synthesis either since the H_2/CO ratio of synthesis gas produced from steam reforming is usually larger than 3. Although methane partial oxidation produces synthesis gas with a H_2/CO ratio of 2, methane partial oxidation is difficult to control due to its exothermic feature and is dangerous and expensive due to the handling of pure oxygen. Tri-reforming, however, is expected to readily produce synthesis gas with the desired H_2/CO ratios of 1.5 ~ 2 by manipulating tri-reforming reactant compositions under relatively mild reaction conditions.

Unlike steam reforming, CO_2 reforming, or methane partial oxidation, tri-reforming has not been systematically studied. The concept of tri-reforming using power plant flue gas was first proposed by Song in 1999 [1,9]. Before 1999, several papers were published on the study of combined CO_2 reforming and partial oxidation reaction [10-12] and simultaneous steam and CO_2 reforming of methane in the presence of oxygen [13]. The results in these papers have indicated that combined reforming is feasible. However, the new tri-reforming process still faces a number of challenges. The future challenges include, for example, effective conversion of CO_2 in the presence of O_2 and H_2O ; the heat management; the minimization of the effect of SO_x and NO_x in flue gas on tri-reforming process; the management of inert gas N_2 in flue gas; and the integration of new process into power plants. The tasks in the current work of tri-reforming include the computational study of equilibrium properties of tri-reforming at various feedstock compositions and reaction conditions, the design of operation parameters, and the development of catalysts tailored for tri-reforming. In a real tri-reforming reaction, steam, CO_2 , and O_2 all compete to react with methane over catalysts. Improvement of CO_2 conversion in the presence of steam and O_2 would depend on the catalysts and reaction conditions.

Experimental

Computational Analysis. The theoretical analysis was based on thermodynamic calculations. The purpose of this analysis is to establish thermodynamic equilibrium conversions of reactants, equilibrium product distributions under different reaction conditions (such as feedstock compositions, temperatures, and pressures) in tri-reforming reaction system.

The equilibrium compositions were calculated based on the principle of atom and mass balance and Gibbs Energy Minimization Method (GEMM). Before calculation, it was critical to identify stable reactants and products in the reaction system. The calculation employed HSC Chemistry software developed by Outokumpu Research Oy, Finland.

Catalyst preparation. Catalysts studied in this work included 8 wt% Ni and 2 wt% Pt catalysts supported on Ce-Zr oxides with or without CaO or MgO promoters. Ce-Zr oxides were prepared according to the method of "soft chemistry" [14]. Zirconium n-propoxide ($\text{Zr}(\text{OC}_3\text{H}_7)_4$) dissolved in 20 ml of isopropyl alcohol was gradually added into an aqueous solution (20ml) of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, leading to the immediate hydrolysis and the formation of a pseudo gel. The pseudo gel was dried at 60°C for 1 h and then at 120°C overnight. The dried sample was finally calcined in air at 870°C for 4 h and ready for use as a support.

Ni and Pt catalysts supported on Ce-Zr oxides were prepared by wet impregnation. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot x\text{H}_2\text{O}$ (MW = 334.12) was dissolved in 5 ml of H_2O . Ce-Zr oxide powder was then added into the solution under stirring. The mixture was dried at 60°C overnight, followed by calcination at 870°C for 4 h. The calcined sample was then pressed into disks and crushed and sieved. The particles between 18-35 meshes were collected for use

in reaction test. When preparing MgO or CaO promoted catalysts, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in the same solution as $\text{Ni}(\text{NO}_3)_2$ or $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ and followed the same procedures as described above.

Tri-reforming experiments. The tri-reforming reaction was studied in a fixed-bed reactor at 850°C under 1 atm. The reactor was made of an Inconel 800H alloy tube with the dimension of 0.54" o.d., 0.375" i.d., and 16" in length. In each tri-reforming, about 0.1 g of catalyst sample was placed in the middle section of the reactor. The reactor was interfaced with GC by a ten-port gas sampling valve, which enables online product analysis. The GC included a packed silica gel column, a molecular sieve column, and a TCD detector. Before each reaction the catalyst was reduced in H_2 following the temperature program: keeping the reactor temperature at 100°C for 15 minutes, at 450°C for 75 minutes, and at 850°C for 10 minutes with a temperature ramp of 12°C/min. Then H_2 was stopped and the reactor temperature was kept at 850°C under Ar flow for another 20 minutes. Steam was first introduced into the reactor. After 20 minutes of steam flow (0.02 ml(l)/min), CH_4 , CO_2 , and O_2 were then introduced into the reactor. The flow rates of CH_4 , CO_2 , and O_2 were maintained by mass flow controllers (Brooks Instruments Corporation, USA); steam flow was controlled by an ISCO liquid pump. The reaction effluent except steam was analyzed by an on-line GC in every 30 minutes during a time-on-stream (TOS) period of 300 minutes. Steam was condensed before the GC.

Results and Discussion

It is expected that steam reforming, CO_2 reforming, and methane oxidation take place simultaneously in tri-reforming system. Table 1 compares equilibrium methane conversions, CO_2 and steam conversions, and H_2/CO ratios in steam reforming, CO_2 reforming, and combined CO_2 and steam reforming with the $(\text{CO}_2 + \text{H}_2\text{O})/\text{CH}_4$ ratio of 1. When steam is gradually replaced by CO_2 , H_2/CO ratios in products decrease monotonically from 3.06 in steam reforming to 1.03 in CO_2 reforming at 850°C and 1 atm while methane conversions and CO_2 conversions have only minor changes.

Table 1. Equilibrium H_2/CO Ratios and Equilibrium Conversions of Methane, Steam, and CO_2 at 850°C and 1 atm

	CH_4 Conv. (%)	CO_2 conv. (%)	Steam conv. (%)	H_2/CO ratio
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2$ =1:1:0	94.0	-	95.4	3.06
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2$ =1:0.75:0.25	94.9	91.3	93.1	2.25
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2$ =1:0.5:0.5	95.8	93.7	88.7	1.66
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2$ =1:0.25:0.75	96.6	94.3	76.4	1.32
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2$ =1:0:1	97.4	95.0	-	1.03
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2:\text{O}_2$ =1:0.475:0.475:0.1	97.9	87.0	77.0	1.67
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2:\text{O}_2$ =1:0.45:0.45:0.2	99.0	75.2	56.0	1.69
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2:\text{O}_2$ =1:0.375:0.375:0.5	99.8	28.4	-29.0	1.71
$\text{CH}_4:\text{H}_2\text{O}:\text{CO}_2:\text{O}_2$ =1:1:1:0.1	99.8	53.1	26.7	1.48

The calculation also predicts a decrease of steam conversions with increasing CO_2 and O_2 concentrations in the feed.

When O_2 is introduced, the ratio of $(\text{CO}_2 + \text{H}_2\text{O} + 0.5\text{O}_2)/\text{CH}_4$ is kept at 1 for comparison with steam reforming, CO_2 reforming,

and combined reforming (Table 1). Although both CO_2 and steam conversions decrease with O_2 concentrations in the tri-reforming system, steam conversions decrease more dramatically than CO_2 conversions. This may be contributed to the reverse water gas shift reaction at high temperatures. Methane conversions only have a slight increase (close to 100%) with the increase of O_2 and a constant H_2/CO ratio is predicted with the addition of O_2 .

When the same amount of CO_2 and H_2O is present in tri-reforming as in the cases of $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}:\text{O}_2=1:0.475:0.475:0.1$ and $\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}:\text{O}_2=1:1:1:0.1$ (Table 1), CO_2 show higher equilibrium conversions (87% and 53.1%, respectively) than the steam conversions (77% and 26.7%, respectively).

Although thermodynamic analysis predicts CO_2 is more preferably converted than steam when same amounts of CO_2 and steam are present in tri-reforming system, one of the major challenges in the study of tri-reforming is the development of new catalysts that are able to efficiently convert CO_2 in the presence of H_2O and O_2 . We have prepared and tested a number of Ni and Pt-based catalysts. Some of the preliminary results are listed in Table 2.

Table 2. Experimental Results of Tri-reforming at 850°C and 1 atm ($\text{CH}_4:\text{CO}_2:\text{H}_2\text{O}:\text{O}_2=1:1:1:0.1$)

	CH_4 Conv. (%)	CO_2 conv. (%)	H_2/CO ratio
8%Ni/Ce-Zr-O	77.0	26.9	1.60
8%Ni/CaO/Ce-Zr-O	86.2	36.6	1.48
8%Ni/MgO/Ce-Zr-O	89.1	38.8	1.49
2%Pt/ Ce-Zr-O	80.4	36.2	1.44
2%Pt/CaO/Ce-Zr-O	64.5	26.5	1.52
2%Pt/MgO/Ce-Zr-O	83.5	32.7	1.57
Equilibrium values	99.8	53.1	1.48

Note: all the experimental data in this table are average values during TOS of 300 minutes.

These experimental results show that CaO and MgO promote methane and CO_2 conversions over Ni-based catalysts although methane and CO_2 conversions over these catalysts are still lower than those predicted from thermodynamic analysis. On the contrary, CaO and MgO in Pt-based catalyst lower CO_2 conversions. These results indicate that catalysts still play an important role in tri-reforming. More catalysts are under investigation.

Conclusions

Equilibrium properties of tri-reforming under different conditions were analyzed by thermodynamics. O_2 in tri-reforming system could lead to the decrease of both CO_2 and steam conversions. CO_2 usually has a higher equilibrium conversion than steam when same amounts of steam and CO_2 co-exist in tri-reforming.

To achieve higher CO_2 conversions in catalytic tri-reforming of methane, a tailored catalyst for tri-reforming is desired.

Acknowledgement. The authors are grateful for the financial support from National Energy Technology Laboratory, US DOE (UCR Innovative Concepts Program, DE-FG26-00NT40829) and Department of Energy and Geo-Environmental Engineering (Graduate assistantship to WP) at Penn State University.

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